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The validity of L-F approximation method in the determination of molecular force fields

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Recently proposed L-F approximation method by Pandey *et al* has been applied to evaluate symmetrized force constants for sixteen complexes belonging to $XY_6(O_h)$, $XY_4(T_d)$ and $XY_4(D_{4h})$ point groups. These constants are compared with the exact or pseudo-exact force constants, recently reported in literature. The validity of L-F approximation in calculating the force constants for molecules of the type XY_n where $M_x > M_y$ or $M_x < M_y$ has been examined.

1. INTRODUCTION

The significance of additional experimental data such as : isotopic shifts, Coriolis coupling constants, mean vibrational amplitudes, rotational distortion constants, relative Raman intensities, inertia defects and *l*-doubling data together with the fundamental vibrational frequencies is well recognized in the determination of unique and unambiguous set of force constants. On account of the development in instrumental and computational techniques, this field has attracted considerable attention in recent years. As a result much progress has been made in the study of reliable intramolecular force fields for a wide variety of molecules and ions. It is, therefore, now possible to test the validity of approximation methods in the study of molecular force fields. The objective of the present investigation is to examine the validity of the L-F approximation method (Pandey *et al* 1976) in the light of current information available in literature. For this purpose we have selected twelve complexes and four molecules belonging to $XY_6(O_h)$, $XY_4(T_d)$ and $XY_4(D_{4h})$ point groups.

2. RESULTS AND DISCUSSION

The results of the computed symmetrized force constants for systems belonging to different point groups are presented in Table 1 along with the fundamental frequencies, used in computations. For examining the validity of the L-F approximation method (Pandey *et al* 1976) the exact or pseudo-exact force constants for the systems under present study are also included in Table 1. As can be seen from Table 1 the force constants obtained using the present method (Pandey *et al* 1976) are physically meaningful and in all cases are in close agreement with their exact or pseudo-exact values. This shows that the L-F approxi-

Table 1. Comparison of Coriolis constants and symmetrized force constants for some XY_n type complexes with exact or pseudo-exact force consants

Complex	Wave Number (in $10^2.m^{-1}$)	Force Constants (in $10^2 Nm^{-1}$) F_{11}	F_{12}	F_{22}	Method	Ref.
$SnCl_6^{2-}$ ^{116}Sn	$\nu_1(F_{1u}) = 323{\cdot}0$	$1{\cdot}45 \pm 0{\cdot}16$	$0{\cdot}13 \pm 0{\cdot}09$	$0{\cdot}18 \pm 0{\cdot}01$	Isotope Shifts	*a*
	$\nu_2(F_{1u}) = 172{\cdot}0$	1·45	0·13	0·18	L-F Approx.	PW
$PdCl_6^{2-}$ ^{104}Pd	$\nu_1(F_{1u}) = 358{\cdot}3$	$1{\cdot}71 \pm 0{\cdot}22$	$0{\cdot}14 \pm 0{\cdot}14$	$0{\cdot}18 \pm 0{\cdot}01$	Isotope Shifts	*a*
	$\nu_2(F_{1u}) = 175{\cdot}0$	1·68	0·13	0·18	L-F Approx.	PW
$TeCl_6^{2-}$	$\nu_0(F_{1u}) = 260$	$0{\cdot}98 \pm 0{\cdot}14$	$0{\cdot}10 \pm 0{\cdot}08$	$0{\cdot}14 \pm 0{\cdot}01$	Isotope Shifts	*a*
	$\nu_2(F_{1u}) = 150$	0·96	0·085	0·14	L-F Approx.	PW
SnF_6^{2-}	$\nu_1(F_{1u}) = 556$	$2{\cdot}69 \pm 0{\cdot}16$	$0{\cdot}16 \pm 0{\cdot}14$	$0{\cdot}34 \pm 0{\cdot}01$	Isotope Shifts	*a*
	$\nu_2(F_{1u}) = 300$	2·68	0·145	0·34	L-F Approx.	PW
$HfCl_6^{2-}$	$\nu_1(F_{1u}) = 275$	$1{\cdot}27 \pm 0{\cdot}21$	$0{\cdot}07 \pm 0{\cdot}15$	$0{\cdot}14 \pm 0{\cdot}03$	Isotope Shifts	*a*
	$\nu_2(F_{1u}) = 145$	1·17	0·07	0·14	L-F Approx.	PW
$PbCl_6^{2-}$	$\nu_1(F_{1u}) = 258$	$1{\cdot}06 \pm 0{\cdot}21$	$0{\cdot}06 \pm 0{\cdot}14$	$0{\cdot}13 \pm 0{\cdot}03$	Isotope Shifts	*a*
	$\nu_2(F_{1u}) = 137$	1·06	0·06	0·13	L-F Approx.	PW
$SnCl_4$ ^{116}Sn	$\nu_1(F_2) = 411{\cdot}3$	$2{\cdot}55 \pm 0{\cdot}03$	$0{\cdot}08 \pm 0{\cdot}02$	$0{\cdot}107 \pm 0{\cdot}001$	Isotope Shifts	*b*
	$\nu_2(F_2) = 127{\cdot}5$	2·52	0·06	0·106	L-F Approx.	PW
^{35}Cl	$\zeta_3 = 0{\cdot}26 \pm 0{\cdot}05$		$\zeta_4 = 0{\cdot}22 \pm 0{\cdot}05$		Exptl.	*c*
	$\zeta_3 = 0{\cdot}28$		$\zeta_4 = 0{\cdot}21$		L-F Approx.	PW
$GeCl_4$ ^{74}Ge	$\nu_3(F_2) = 461{\cdot}3$	$2{\cdot}73 \pm 0{\cdot}13$	$0{\cdot}13 \pm 0{\cdot}08$	$0{\cdot}170 \pm 0{\cdot}003$	Exptl.	*d*
	$\nu_1(F_2) = 171{\cdot}3$	2·77	0·12	0·17	L-F Approx.	PW
^{35}Cl	$\zeta_3 = 0{\cdot}38 \pm 0{\cdot}05$		$\zeta_4 = 0{\cdot}08 \pm 0{\cdot}07$		Exptl.	*c*
	$\zeta_3 = 0{\cdot}39$		$\zeta_4 = 0{\cdot}10$		L-F Approx.	PW
$GeBr_4$	$\nu_1(F_2) = 332$	2·25	0·14	0·13	Raman band Cont.	*e*
	$\nu_2(F_2) = 111$	2·261	0·14	0·13	L-F Approx.	PW
RuO_4 ^{99}Ru	$\nu_1(F_2) = 921$	$6{\cdot}49 \pm 0{\cdot}05$	$0{\cdot}07 \pm 0{\cdot}05$	$0{\cdot}381 \pm 0{\cdot}002$	Exptl.	*f*
	$\nu_2(F_2) = 336$	6·64	0·129	0·39	L-F Approx.	PW
	$\zeta_3 = 0{\cdot}02 \pm 0{\cdot}02$				Exptl.	*f*
	$\zeta_3 = 0{\cdot}18 \pm 0{\cdot}05$		$\zeta_4 = 0{\cdot}31 \pm 0{\cdot}03$		Exptl.	*c*
	$\zeta_3 = 0{\cdot}18$		$\zeta_4 = 0{\cdot}32$		L-F Approx.	PW

Table 1 : Comparison of Coriolis Constants and symmetrized force constants for same XY_n type complexes with exact or pseudo-exact force constants (*Contd.*)

Complex	Wave Number (in $10^2.m^{-1}$)	Force Constants (in $10^2 Nm^{-1}$)			Method	Ref.
		F_{11}	F_{12}	F_{22}		
$[Cr(NH_3)_6]^{3+}$						
^{50}Cr	$\nu_1(F_{1u}) = 471{\cdot}0$	$1{\cdot}59 \pm 0{\cdot}09$	$0{\cdot}26 \pm 0{\cdot}08$	$0{\cdot}21 \pm 0{\cdot}02$	PE-PMM	*a*
	$\nu_2(F_{1u}) = 270{\cdot}0$	1·42	0·14	0·20	L-F Approx.	PW
		1·45	0·16	0·20	$L_{12} = 0$	
		1·72	0·50	0·30	$L_{21} = 0$	
$[Co(NH_3)_6]^{3+}$						
	$\nu_1(F_{1u}) = 474{\cdot}7$	$1{\cdot}78 \pm 0{\cdot}03$	$0{\cdot}55 \pm 0{\cdot}04$	$0{\cdot}43 \pm 0{\cdot}03$	PE-PMM	*g*
	$\nu_2(F_{1u}) = 331{\cdot}0$	1·54	0·63	0·55	L-F Approx.	PW
		1·60	0·23	0·31	$L_{12} = 0$	
		1·78	0·48	0·38	$L_{21} = 0$	
$[Ni(NH_3)_6]^{2+}$						
^{58}Ni	$\nu_1(F_{1u}) = 335{\cdot}2$	$0{\cdot}87 \pm 0{\cdot}04$	$0{\cdot}18 \pm 0{\cdot}05$	$0{\cdot}15 \pm 0{\cdot}04$	PE-PMM	*a*
	$\nu_2(F_{1u}) = 217{\cdot}0$	0·76	0·08	0·14	L-F Approx.	PW
		0·78	0·10	0·13	$L_{12} = 0$	
		0·89	0·24	0·17	$L_{21} = 0$	
$^{1}Zn(NH_3)_4]^{2+}$						
^{64}Zn	$\nu_1(F_2) = 412$	$1{\cdot}38 \pm 0{\cdot}08$	$0{\cdot}19 \pm 0{\cdot}14$	$0{\cdot}10 \pm 0{\cdot}04$	PE-PMM	*a*
	$\nu_2(F_2) = 156$	1·28	0·04	0·08	L-F Approx.	PW
$[Cu(NH_3)_4]^{2+}$						
^{63}Cu	$\nu_1(E_u) = 426$	$1{\cdot}14 \pm 0{\cdot}23$	$-0{\cdot}04 \pm 0{\cdot}10$	$0{\cdot}25 \pm 0{\cdot}07$	PE-PM	*h*
	$\nu_2(E_u) = 256$	1·225	−0·10	0·245	L-F Approx.	PW
		$1{\cdot}29 \pm 0{\cdot}09$	$-0{\cdot}17 \pm 0{\cdot}09$	$0{\cdot}25 \pm 0{\cdot}02$	PE-PMM	*a*
$[Pd(NH_3)_4]^{2+}$						
^{104}Pd	$\nu_1(E_u) = 495{\cdot}0$	$1{\cdot}93 \pm 0{\cdot}14$	$-0{\cdot}175 \pm 0{\cdot}17$	$0{\cdot}34 \pm 0{\cdot}04$	PE-PMM	*a*
	$\nu_2(E_u) = 291{\cdot}0$	1·88	−0·10	0·34	L-F Approx.	PW

a—Müller *et al* (1975); *b*—Königer and Müller (1975); *c*—Müller and Königer (1976); *d*. Debabcioglu *et al* (1968); *e*. Clark and Rippon (1972); *f*. Müller and Krebs (1968); *g*. Schmidt and Müller (1974); *h*—Cyvin *et al* (1976).

PE-PMM—Pseudo-Exact Point Mass Model.
PW—Present Work.

mation method is valid in these cases. It is also noted that the computed force constants for $SnCl_4$, $GeCl_4$ and RuO_4 reproduce the Coriolis coupling constants which are in excellent agreement with the experimental data (Müller & Königer 1976, Müller & Krebs 1968). This also supports our present approach.

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